Disentangling the ligand and electronic structure in $KVPO_4F_{1-x}O_x$ positive electrode materials by Valence-to-Core X-ray emission spectroscopy

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Supplementary Information

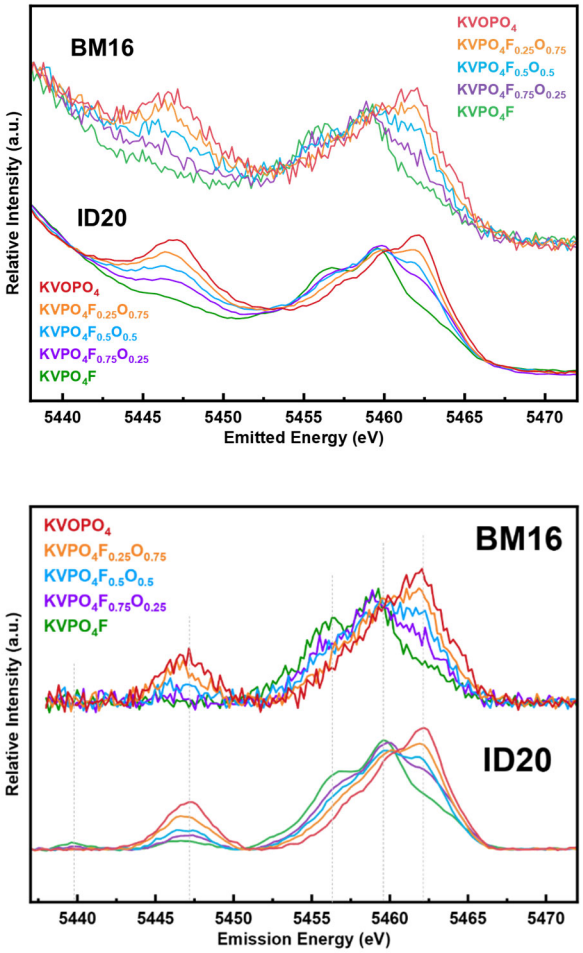


Figure S1. Vanadium VtC XES spectra from BM16 and ID20 at the European Synchrotron and Radiation Facility (ESRF) showing reproducibility of the results from the measurements performed. Raw spectra obtained (top) and baseline-subtracted spectra (bottom)

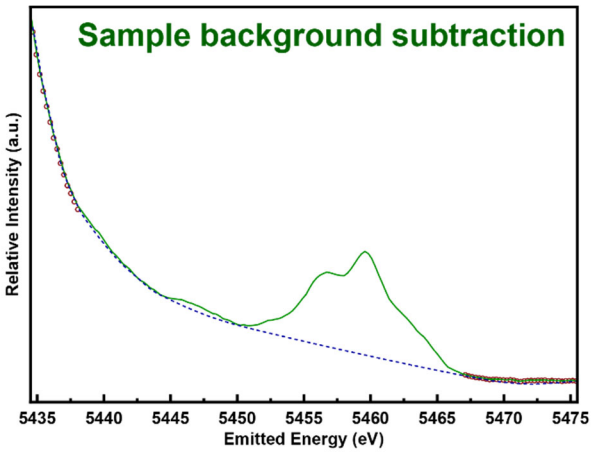


Figure S2. VtC data background subtraction[1]

Table S1. $KVPO_4F$ input file for the FDMNES calculation

```
! FDMNES indata file
! Calculation for the V VtC_Kbeta KVPO4F
! Finite difference method calculation with convolution

 Filout
   pristine_cell/pristine_vfp/pristine_vfp

 Range     ! Energy range of calculation (eV)
 -40. 0.2 -10 0.1 -5 0.05 0. 0.1 5 0.2 10. .5 40. 1 60. ! first energy, step, intermediary
energy, step ..., last energy

 Radius    ! Radius of the cluster where final state calculation is performed
 8.0

 SCF       ! Activation of the self consistent field calculation

 Green     ! Inclusion of the green function

 Density_all   ! Densities of state results

 Edge
 K

 XES

 Z_absorber
 23

 Spgroup
 33

 Occupancy

 Crystal_t
    12.8223 6.39721 10.6203 90 90 90  ! Cell parameters
 !Atoms
 19  0.3802  0.7788  0.3018 1.02      !Potassium
 19  0.1044  0.6972  0.0590 0.97
 23  0.3854  0.4967  0      1.00      !Vanadium
 23  0.2469  0.2514  0.2469 1.00
 15  0.4988  0.3311  0.2501 1.00      !Phosphorus
 15  0.1817  0.4991  0.4991 1.00
 8   0.4848  0.4865  0.1406 1.00      !Oxygen
 8   0.5122  0.4682  0.3691 1.00
 8   0.4008  0.1959  0.2689 1.00
 8   0.5955  0.1935  0.2286 1.00
 8   0.1112  0.3107  0.5292 1.00
 8   0.1127  0.6910  0.4722 1.00
 8   0.2501  0.5377  0.6163 1.00
 8   0.2566  0.4580  0.3888 1.00
 9   0.2706  0.5230  0.8788 1.00      !Fluorine
 9   0.2716  0.4777  0.1266 1.00


!!!Convolution keyword : broadening with a width increasing versus energy as an arctangent

 Estart
 -20

 Efermi
 -5.0

 Convolution
 42 11 10

 Gamma_hole
 0.7

 Gaussian
 1.0

 End
```

Table S2. $KVOPO_4$ input file for the FDMNES calculation

```
! FDMNES indata file
! Calculation for the V VtC_Kbeta KVOPO4
! Finite difference method calculation with convolution

 Filout
   pristine_cell/pristine_vop/pristine_vop

 Range     ! Energy range of calculation (eV)
 -40. 0.2 -10 0.1 -5 0.05 0. 0.1 5 0.2 10. .5 40. 1 60. ! first energy, step, intermediary
energy, step ..., last energy

 Radius    ! Radius of the cluster where final state calculation is performed
 8.0

 SCF       ! Activation of the self consistent field calculation

 Green     ! Inclusion of the green function

 Density_all   ! Densities of state results

 Edge
 K

 XES

 Z_absorber
 23

 Spgroup
 33

 Occupancy

 Crystal_t
 12.7618 6.3654  10.5126 90 90 90    !Cell parameters
 !Atoms
 19  0.3820  0.3820  0.7827 1.04      !Potassium
 19  0.1030  0.7047  0.0596 0.96
 23  0.3765  0.4960  0      1.00      !Vanadium
 23  0.2478  0.2739  0.2390 1.00
 15  0.4961  0.3307  0.2490 1.00      !Phosphorus
 15  0.1805  0.4980  0.5052 1.00
 8   0.4830  0.4820  0.1360 1.00      !Oxygen
 8   0.5120  0.4680  0.3680 1.00
 8   0.3995  0.1910  0.2720 1.00
 8   0.5936  0.1900  0.2330 1.00
 8   0.1100  0.3060  0.5290 1.00
 8   0.1090  0.6860  0.4740 1.00
 8   0.2500  0.5370  0.6210 1.00
 8   0.2570  0.4590  0.3940 1.00
 8   0.2870  0.5280  0.8820 1.00      !Oxygen vanadyl oxygen
 8   0.2680  0.4630  0.1320 1.00


!!!Convolution keyword : broadening with a width increasing versus energy as an arctangent

 Estart
 -20

 Efermi
 -5.0

 Convolution
 42 11 10

 Gamma_hole
 0.7

 Gaussian
 1.0

 End
```

Table S3. Calculated bond valence sum (BVS) for all pristine and reference materials. [2]

	V_{cis}	V_{trans}	$V_{average}$
$KVPO_4F$	3.10	2.96	**3.03**
$KVPO_4F_{0.75}O_{0.25}$	3.33	3.18	**3.25**
$KVPO_4F_{0.5}O_{0.5}$	3.57	3.43	**3.50**
$KVPO_4F_{0.25}O_{0.75}$	3.85	3.62	**3.74**
$KVOPO_4$	4.05	3.86	**3.96**
$Na_3V_2(PO_4)_3$			**3.07**
$Na_1V_2(PO_4)_3$			**4.05**
$NaVOPO_4$			**3.90**
β-$VOPO_4$			**5.26**

Bonding	***Ro***	***b***
V^{III}-$O^{(-2)}$	1.743	0.37
V^{III}-$F^{(-1)}$	1.702	
V^{IV}-$O^{(-2)}$	1.784	
V^{IV}=$O^{(-2)}$	1.735	
V^{IV}-$F^{(-1)}$	1.700	
V^{V}-$O^{(-2)}$	1.803	

$$BVS = \sum_{R_{exp}=1}^{6} e^{\frac{R_o - R_{exp}}{b}}$$

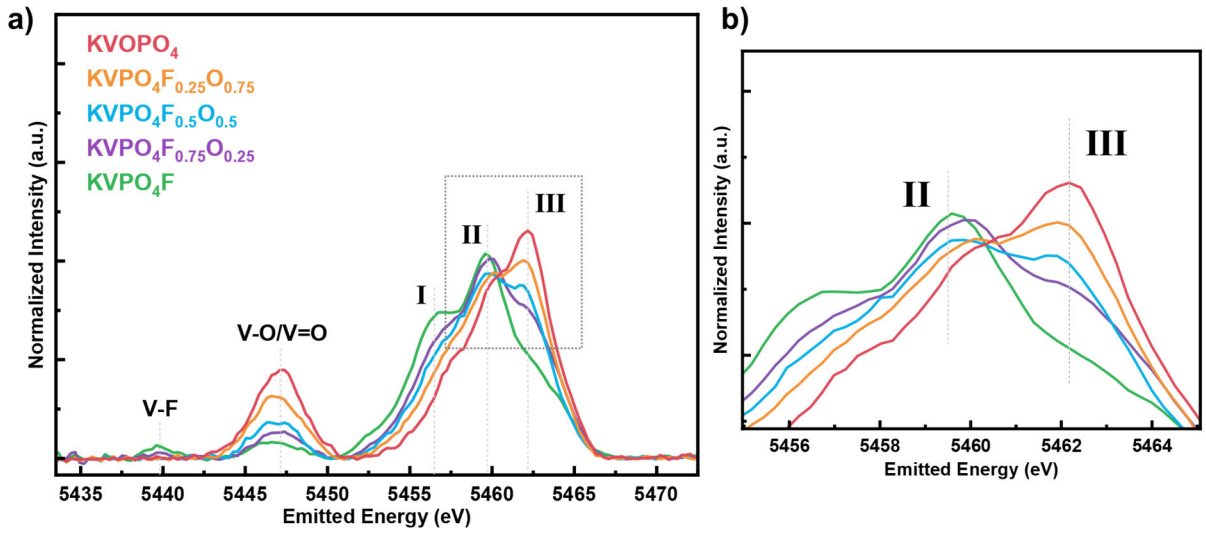


Figure S3. a) Normalized Kβ VtC XES emission lines of $KVPO_4F_{1-x}O_x$ (x = 0, 0.25, 0.5, 0.75, 1) and b) highlighted energy range where the isosbestic point of the five spectra lies.

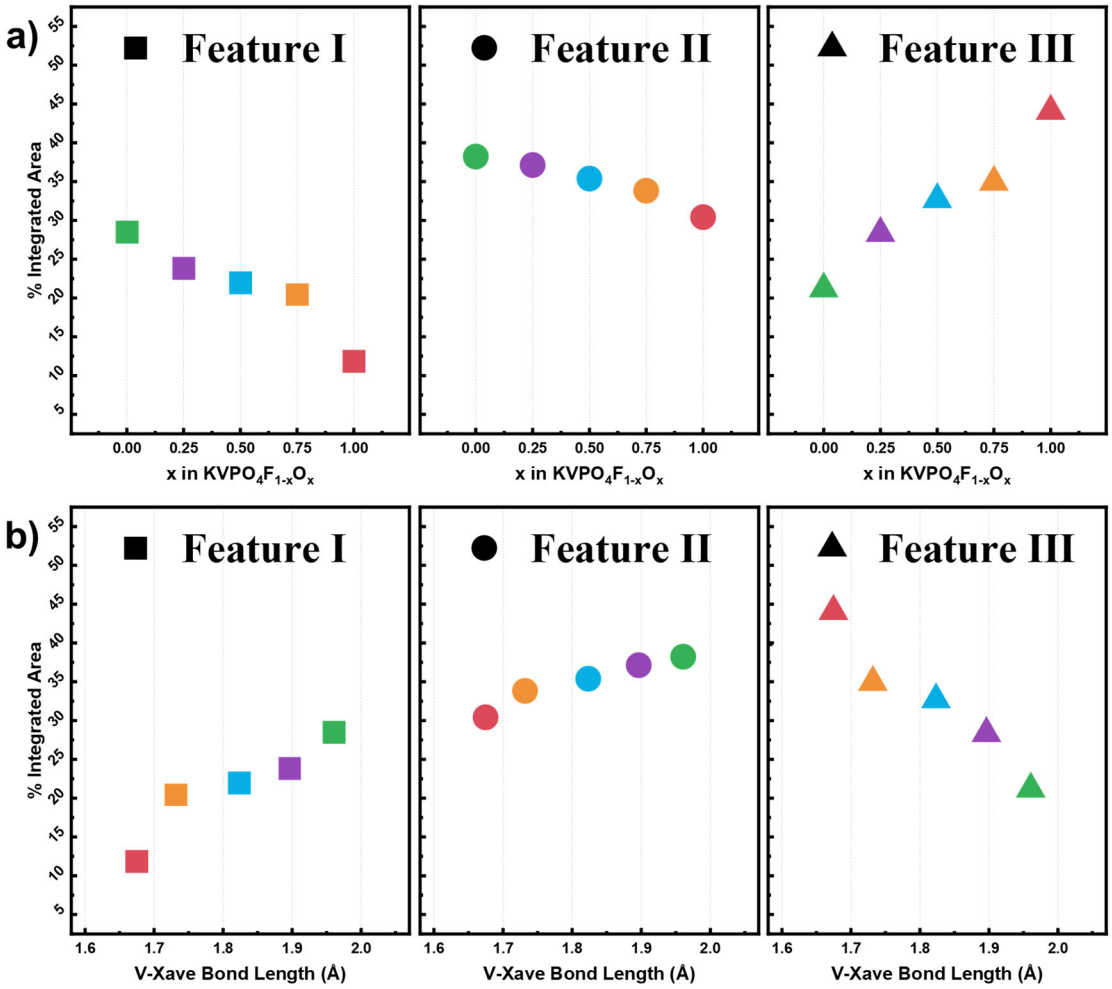


Figure S4. Graphical representation of the changes in the area of the contributions for features I, II, and III for the $KVPO_4F_{1-x}O_x$ series of materials: (a) correlation between composition x vs integrated area and (b) correlation between V-X_{ave} bond length vs integrated area.

Table S4. Curve-fitting parameters and calculated contributions

$KVPO_4F$	Feature	Position, eV	FWHM	Area, %	Gaussian FWHM	Lorentzian FWHM	Weighted Sum of Squared Residuals
V-O-P_O 2s*/2p	r_i	5454.00	3.206	8.60	3.008	0.361	
V-O-P_O 2p	**I**	5456.61	2.848	28.52	2.672	0.321	
V-F-V_F 2p, V-O-P_O 2p	**II**	5459.57	2.764	**38.23**	**2.593**	**0.312**	2.53×10^{-6}
V-O-P_O 2p	**III**	5464.65	2.059	**21.18**	**1.932**	**0.232**	
V-O-P_O 2p	r_{ii}	5462.31	3.262	3.48	3.060	0.368	

$KVPO_4F_{0.75}O_{0.25}$	Feature	Position, eV	FWHM	Area, %	Gaussian FWHM	Lorentzian FWHM	Weighted Sum of Squared Residuals
V-O-P_O 2s*/2p	r_i	5454.39	2.873	5.58	2.695	0.324	
V-O-P_O 2p	**I**	5456.81	2.990	23.82	2.805	0.337	
V-F-V_F 2p, V=O-V_O 2p σ/π	**II**	5459.66	2.900	**37.14**	**2.721**	**0.327**	1.83×10^{-6}
V=O-V_O 2p π	**III**	5462.35	3.100	**28.34**	**2.909**	**0.349**	
V-O-P_O 2p	r_{ii}	5464.36	2.265	5.12	2.125	0.255	

$KVPO_4F_{0.5}O_{0.5}$	Feature	Position, eV	FWHM	Area, %	Gaussian FWHM	Lorentzian FWHM	Weighted Sum of Squared Residuals
V-O-P_O 2s*/2p	r_i	5454.60	2.822	5.76	2.648	0.318	
V-O-P_O 2p	**I**	5456.97	2.976	21.97	2.792	0.335	
V-F-V_F 2p, V=O-V_O 2p σ/π	**II**	5459.60	2.901	**35.39**	**2.722**	**0.327**	1.69×10^{-6}
V=O-V_O 2p π	**III**	5462.18	2.881	**32.69**	**2.703**	**0.325**	
V-O-P_O 2p	r_{ii}	5464.32	2.165	4.19	2.031	0.244	

$KVPO_4F_{0.25}O_{0.75}$	Feature	Position, eV	FWHM	Area, %	Gaussian FWHM	Lorentzian FWHM	Weighted Sum of Squared Residuals
V-O-P_O 2s*/2p	r_i	5454.98	2.920	5.45	2.740	0.329	
V-O-P_O 2p	**I**	5457.36	3.012	20.46	2.826	0.339	
V-F-V_F 2p, V=O-V_O 2p σ/π	**II**	5459.87	2.887	**33.83**	**2.709**	**0.325**	1.09×10^{-6}
V=O-V_O 2p π	**III**	5462.30	2.666	**34.94**	**2.501**	**0.300**	
V-O-P_O 2p	r_{ii}	5464.39	1.858	5.32	1.744	0.209	

$KVOPO_4$	Feature	Position, eV	FWHM	Area, %	Gaussian FWHM	Lorentzian FWHM	Weighted Sum of Squared Residuals
V-O-P_O 2s*/2p	r_i	5455.97	3.183	6.90	2.987	0.359	
V-O-P_O 2p	I	5457.61	2.237	11.86	2.099	0.252	
V=O-V_O 2p σ/π	**II**	5459.89	2.602	**30.43**	**2.442**	**0.293**	1.53×10^{-6}
V=O-V_O 2p π	**III**	5462.31	2.633	**44.08**	**2.470**	**0.297**	
V-O-P_O 2p	r_{ii}	5464.55	1.931	6.73	1.812	0.218	

*r_i and r_{ii} are the residual contributions at the low emission energy and high emission energy, respectively, for the fitting procedure.

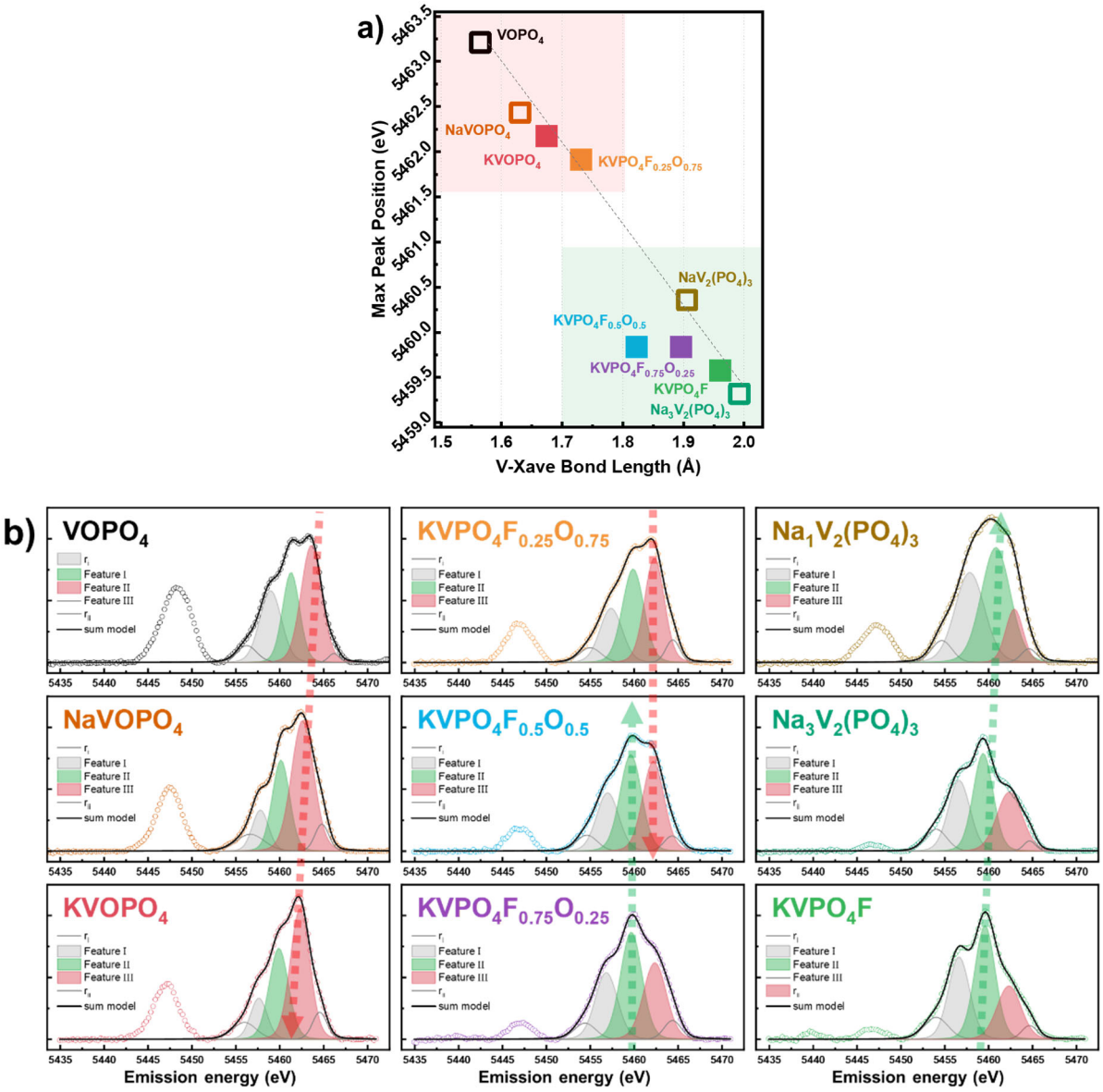
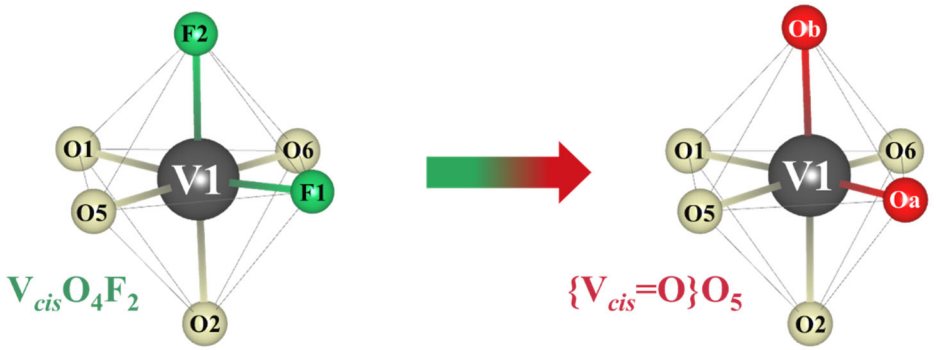


Figure S5. (a) The energy of the absolute maximum peak position of the VtC spectrum at the Kβ$_{2,5}$ region in relation to the average bond length of V=O for vanadyl containing compounds and average bond length of V-O for $NaV_2(PO_4)_3$ and $Na_3V_2(PO_4)_3$ and (b) the experimental spectra of pristine and reference compounds along with the peak deconvolution using five Voigt functions

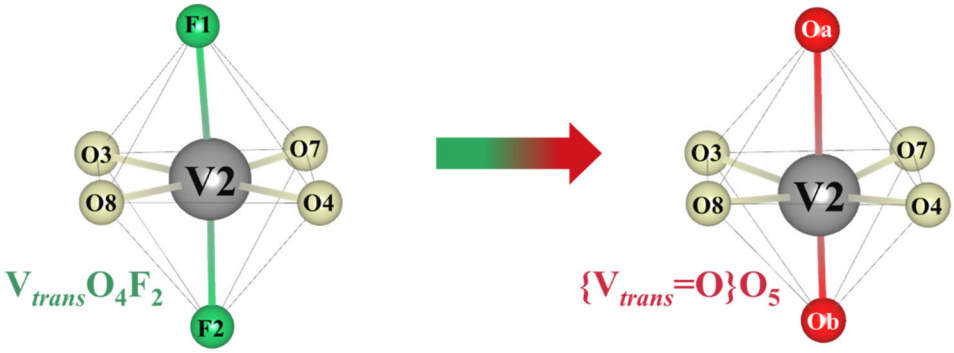
It should be noted that the intensities recorded at the maximum peak position (Feature II or Feature III, depending on the material) for the $KVPO_4F$ and $KVOPO_4$ end members exhibit a linear relationship with $Na_3V_2(PO_4)_3$, $NaV_2(PO_4)_3$, $NaVOPO_4$, and $VOPO_4$ reference materials concerning the average V-X bond lengths, indicating a high correlation between these parameters. However, no linear evolution is observed for compounds with partial compositions in the $KVPO_4F_{1-x}O_x$ series, especially $KVPO_4F_{0.5}O_{0.5}$, which appears as an outlier in the trend mainly due to its mixed nature.

Additionally, a hypothesis can be formulated regarding the general disparity between ionicity and covalency concerning the presence of V-F and V=O bonds, particularly when considering features I and II (mainly feature II) in comparison with feature III. As depicted in Figure S5b, the deconvolution of all compounds (including references and pristine mixed materials) reveals feature III shaded in red, indicating a higher covalent environment, with an arrow pointing downward to signify decreasing covalency (from shorter to longer V=O bond lengths, from $VOPO_4$ to $KVOPO_4$ to $KVPO_4F_{0.5}O_{0.5}$). Conversely, feature II is shaded in green, indicating a more ionic environment, with an arrow pointing upward towards a higher degree of covalency (from $KVPO_4F$ to $NaV_2(PO_4)_3$ to $KVPO_4F_{0.5}O_{0.5}$).

Table S5. Bond lengths obtained from refined XRD patterns (Rietveld method) of the atoms around the (top) cis vanadium site and (bottom) trans vanadium site for $KVPO_4F_{1-x}O_x$ (x = 0, 0.25, 0.5, 0.75, 1) [2]



V_{cis}	$KVPO_4F$	$KVPO_4F_{0.75}O_{0.25}$	$KVPO_4F_{0.5}O_{0.5}$	$KVPO_4F_{0.25}O_{0.75}$	$KVOPO_4$
V1-O1	1.961	1.964	1.964	1.981	1.994
V1-O2	1.928	1.944	1.972	1.978	1.985
V1-O5	2.032	2.046	2.029	2.033	2.008
V1-O6	1.979	1.993	1.979	1.977	1.994
V1-F1/=Oa	1.965	1.885	1.822	1.728	1.683
V1-F2/Ob	1.984	1.972	1.981	1.991	1.981



V_{trans}	$KVPO_4F$	$KVPO_4F_{0.75}O_{0.25}$	$KVPO_4F_{0.5}O_{0.5}$	$KVPO_4F_{0.25}O_{0.75}$	$KVOPO_4$
V2-O3	2.018	1.998	2.016	2.012	2.036
V2-O4	1.983	2.002	1.987	1.984	1.982
V2-O7	1.948	1.957	1.966	1.977	1.943
V2-O8	2.011	1.996	1.986	1.988	2.023
V2-F1/Oa	2.039	2.054	2.086	2.213	2.215
V2-F2/=Ob	1.957	1.908	1.825	1.735	1.666

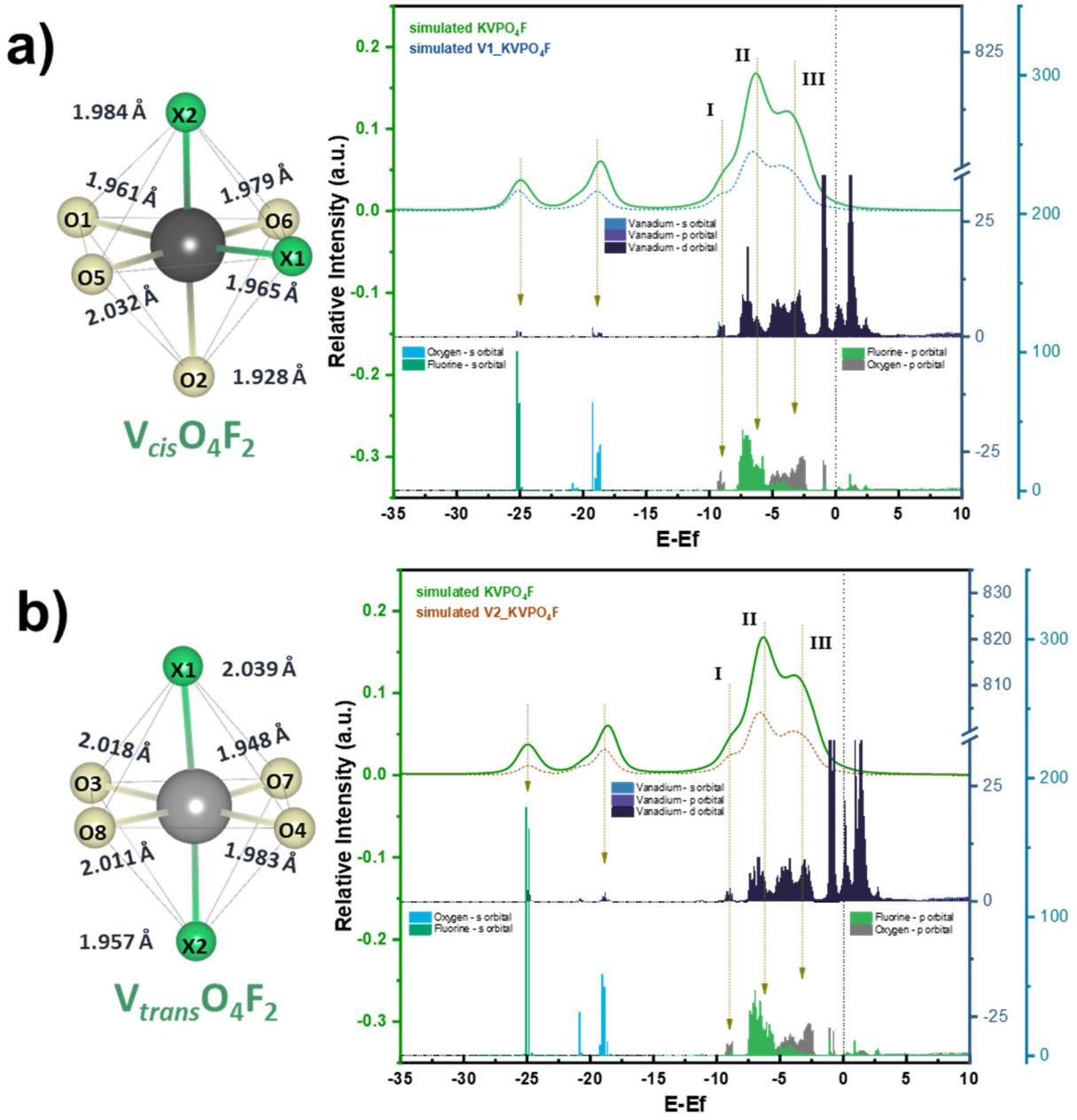


Figure S6. Calculated density of states for the simulated $KVPO_4F$ spectra for a) $V_{cis}O_4F_2$ and b) $V_{trans}O_4F_2$

The density of states (DOS) obtained from the theoretical calculation performed can be deconvoluted to the individual contributions of the two different vanadium sites (V_{cis} and V_{trans}) present in the material.[2] In $KVPO_4F$, it is noticeable that the features for both sites show similar characteristic which is related to the degree of bonding between V-O and V-F.

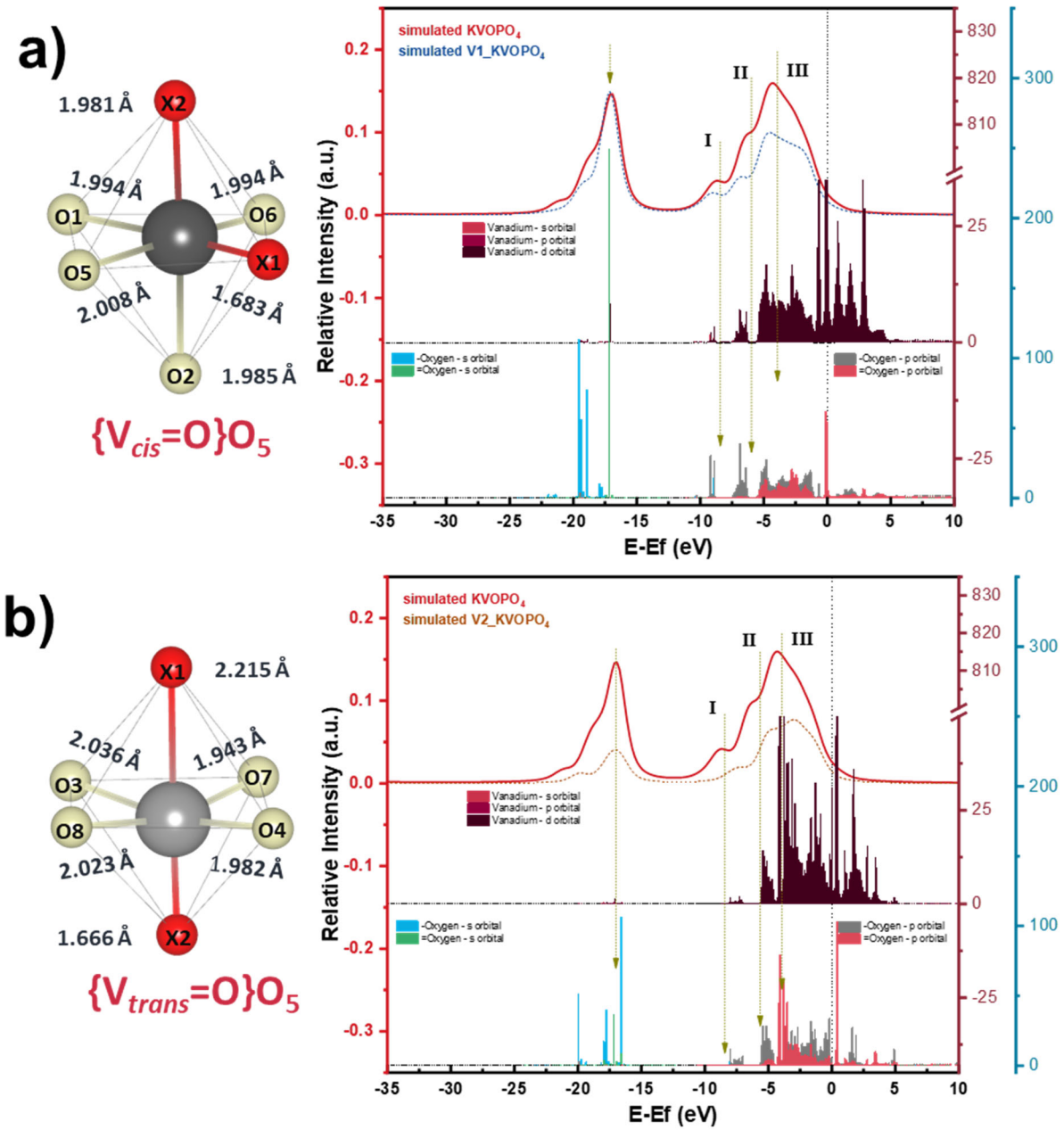


Figure S7. Calculated density of states for the simulated $KVOPO_4$ spectra for b) $\{V_{cis}=O\}O_5$ and b) $\{V_{trans}=O\}O_5$

In contrast with $KVPO_4F$, a much bigger difference is observed for $KVOPO_4$ especially at the $K\beta_{2,5}$ region of both $\{V_{cis}=O\}O_5$ and $\{V_{trans}=O\}O_5$. It can be deduced that due to the different position of the distortion causing vanadyl bonds, the hybridization of molecular orbitals varies and affects the overall electronic structure.

References:

1 E. Gallo and P. Glatzel, *Adv. Mater.*, 2014, **26**, 7730–7746.

2 R. Wernert, L. H. B. Nguyen, E. Petit, P. S. Camacho, A. Iadecola, A. Longo, F. Fauth, L. Stievano, L. Monconduit, D. Carlier and L. Croguennec, *Chem. Mater.*, 2022, **34**, 4523–4535.